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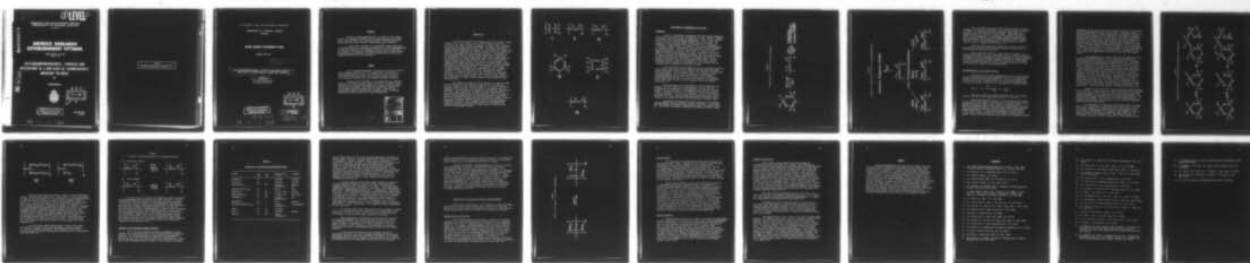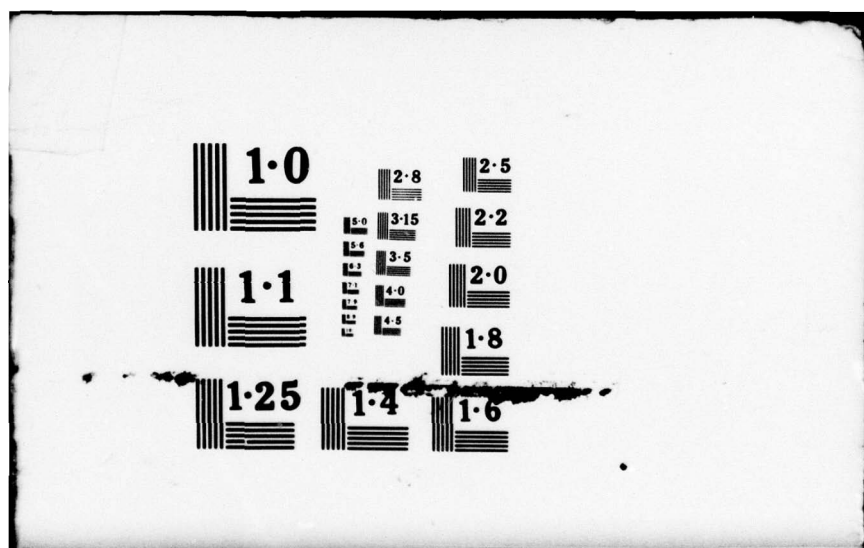JAN 79   J M MCANDLESS

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DREO REPORT NO. 795
DREO R 795

POLY(ORGANOPHOSPHAZENES). SYNTHESIS AND APPLICATIONS OF A NEW CLASS OF TECHNOLOGICALLY IMPORTANT POLYMERS

by

J.M.McAndless

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POLY(ORGANOPHOSPHAZENES). SYNTHESIS AND APPLICATIONS OF A NEW CLASS OF TECHNOLOGICALLY IMPORTANT POLYMERS

by

10 J.M. McAndless

Environmental Protection Section
Protective Sciences Division

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ABSTRACT

The poly(organophosphazenes) are a new class of high polymers based on an "inorganic" backbone of alternating phosphorus and nitrogen atoms. These polymers show considerable promise in meeting materials requirements that cannot be met by conventional organic polymers.

In this report, the history of phosphazene polymer development is briefly reviewed, the synthesis and properties of poly(organophosphazenes) are described and some of the problems associated with their synthesis are outlined. The potential technological applications of these polymers as extreme-service materials, protective coatings, textile products and biomedical materials, are also described.

RÉSUMÉ

Les poly(organophosphazènes) constituent une nouvelle classe de hauts polymères, basée sur un tronc "inorganique" où alternent les atomes de phosphore et d'azote. Les matériaux fabriqués à partir de ces polymères satisferont sans doute à certaines normes de qualité qu'on ne pouvait atteindre avec les polymères organiques ordinaires.
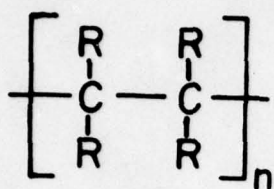
L'historique des polymères de type phosphazène est brièvement passée en revue dans le présent rapport qui décrit la synthèse et les propriétés des poly(organophosphazènes) et souligne certains problèmes associés à leur synthèse. Les applications techniques possibles de ces polymères figurent également dans ce rapport: matériaux qui pourront être soumis à des conditions extrêment sévères, revêtements protecteurs, produits textiles et produits biomédicaux.
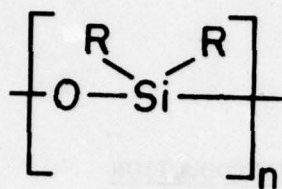
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INTRODUCTION

In spite of the multitude of applications which synthetic organic polymers fulfil, there remains a need for new polymer systems with properties that organic polymers are unable to provide. This is because the presence of carbon atoms in the backbone of conventional polymers (I) places important restrictions on their uses. For example, most organic polymers burn and when used, for example, as textile fibers or construction materials their flammability can only be reduced by the introduction of labile and sometimes toxic flame-retardant compounds. The geometry of the tetrahedral carbon atom and the short length of the carbon-carbon bond can generate a chain stiffness which may preclude polymer elasticity and flexibility over a broad temperature range. Only a few synthetic organic polymers remain flexible when cooled to low temperatures. The backbone carbon atoms constitute a weak link which makes organic polymers susceptable to oxidation or decomposition catalyzed by ultraviolet light and accelerated by high temperatures. The "organic" nature of most synthetic polymers is believed to be responsible for their propensity to dissolve or swell in hydrocarbon fuels, lubricants and organic solvents. In biomedical applications, the construction of replacement body organs, such as artificial heart pumps, synthetic blood vessels, artificial skin, replacement tendons, etc, has been severely hampered by the incompatibility of many organic polymers with body tissues, blood and lymph fluid.
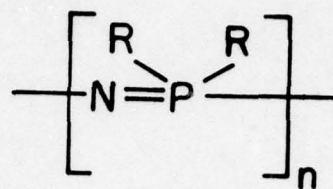
One approach to overcoming the deficiencies of organic polymers is to design polymers that contain no carbon atoms in the backbone. Silicone polymers, or poly(organosiloxanes)(II), are the best recognized examples of this principle. Silicone rubber is now commonly used in applications for which stability, flexibility and biomedical compatibility are needed. Other examples of "inorganic" polymer systems which are used in specialty applications are the polythiazyls (sulfur-nitrogen)(1), thermally stable polymers based on alternating siloxane and carborane units (silicon-boron/carbon)(2) and metal co-ordination polymers. However, the class of inorganic polymers which has received the most extensive development in the past 10 to 15 years is the poly(organophosphazene) system (3,4,5,6)(III). These polymers are based on a backbone which contains alternating phosphorus and nitrogen atoms with substituents attached to the phosphorus atoms.

$$\left[\begin{array}{c} R \\ | \\ -C- \\ | \\ R \end{array} \begin{array}{c} R \\ | \\ -C- \\ | \\ R \end{array}\right]_n \qquad \left[\begin{array}{c} R \quad R \\ \backslash \; / \\ O-Si \\ \end{array}\right]_n \qquad \left[\begin{array}{c} R \quad R \\ \backslash \; / \\ N=P \\ \end{array}\right]_n$$

I   II   III

IV   V

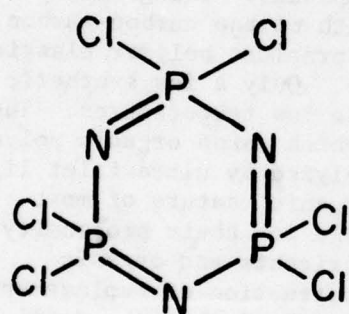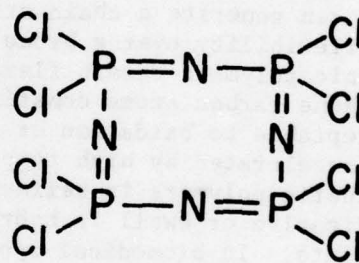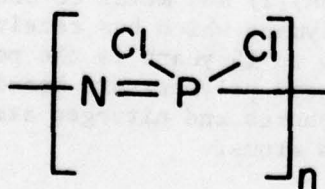$$\left[\begin{array}{c} Cl \quad Cl \\ \backslash \; / \\ N=P \\ \end{array}\right]_n$$

VI

DEVELOPMENT OF PHOSPHAZENE HIGH POLYMERS

BACKGROUND

Cyclic or non-polymeric phosphazenes have been studied extensively since it was first reported over 150 years ago (7) that reaction of ammonia or ammonium chloride and phosphorus pentachloride yields a white, volatile solid, known to be hexachlorocyclotriphosphazene, a cyclic trimer (IV). The cyclic trimer, and other higher cyclics such as the tetramer (V), pentamer etc., when strongly heated, are converted into a transparent, crosslinked rubbery material now referred to as poly(dichlorophosphazene) or "inorganic rubber". This material is not soluble in organic solvents and hydrolyzes slowly in contact with atmospheric moisture to yield ammonium phosphate and phosphoric acid. Thus, the possible use of this rubber as a technological elastomer is severely restricted. Because of the high reactivity of the phosphorus-chlorine bonds, one obvious approach to reducing the hydrolytic instability of "inorganic rubber" was to replace the chlorine atoms with stable organic substituents. However, attempted nucleophilic substitution reactions on the rubber, swollen in solvents such as benzene or tetrahydrofuran, were incomplete and the resulting polymers remained hydrolytically unstable.

Since hexachlorocyclotriphosphazene could be polymerized thermally, it was expected that hydrolytically stable cyclophosphazenes containing organic substituents such as ethoxy, phenoxy, etc. could also be polymerized in the same manner. This alternative route to the synthesis of poly-(organophosphazenes) by the direct polymerization of hexa(organo)-cyclotriphosphazene has met with little success, due to the fact that ring-opening polymerizations of this type are inhibited by thermodynamic factors that result, in part, from the presence of the bulky organic substituents (5).

The breakthrough in the development of useful phosphazene high polymers occurred in 1965 when it was discovered (9,10,11) that the polymerization of hexachlorocyclotriphosphazene (IV) followed a two-step sequence, as shown in Scheme 1. The polymer formed during the initial stages of the reaction (VI) was not crosslinked and was totally soluble in organic solvents. It was not until the latter stages of the reaction when about 70% of the trimer had been consumed, that substantial cross-linking of the polymer occurred to give the insoluble "inorganic rubber".

Nucleophilic substitution reactions carried out on the soluble chlorophosphazene polymer resulted in complete replacement of the halogen and the formation of a series of hydrolytically stable new polymers (9,10, 11). The overall nucleophilic substitution processes are shown in Scheme 2.

CROSSLINKED
POLY(DICHLOROPHOS-
PHAZENE)
"INORGANIC RUBBER"

250°
traces of H$_2$O

$$\left[\begin{array}{c} Cl \\ | \\ N = P \\ | \\ Cl \end{array} \right]_n$$
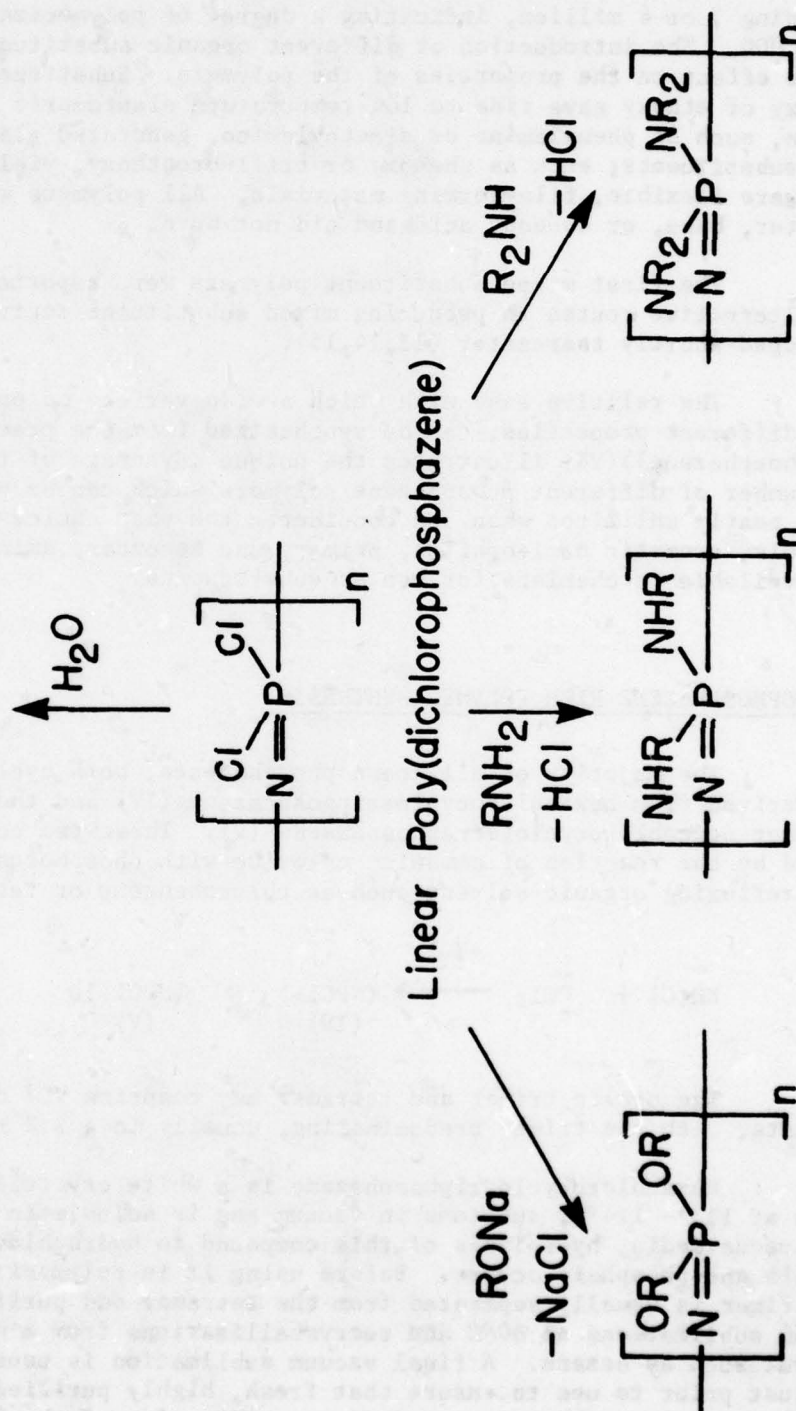
350°   230-250°

SCHEME 1.
Polymerization of Hexachlorocyclotriphosphazene.
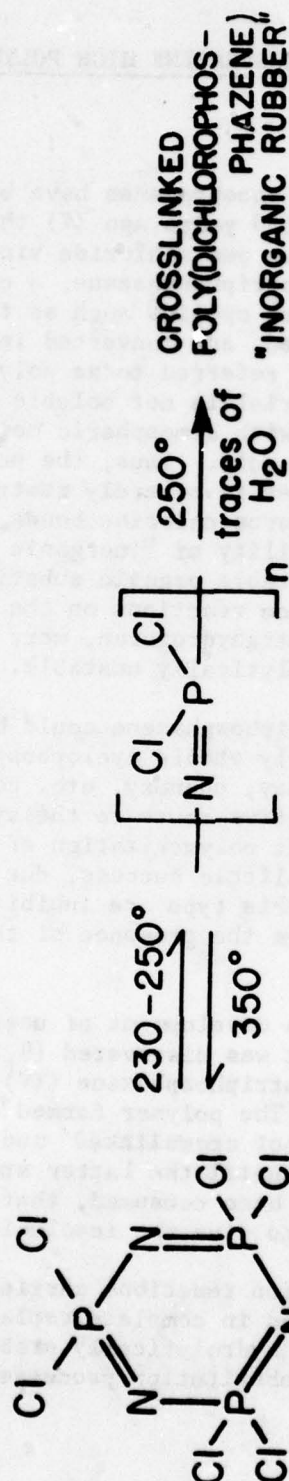
SCHEME 2.

Nucleophilic Substitution of Linear Poly(dichlorophosphazene).

Ammonium Phosphates, Chlorides

Linear Poly(dichlorophosphazene)

The new polymers were found to have molecular weights sometimes exceeding 3 or 4 million, indicating a degree of polymerization in excess of 15,000. The introduction of different organic substituents had a marked effect on the properties of the polymers. Substituents such as methoxy or ethoxy gave rise to low-temperature elastomeric properties. Others, such as phenylamino or dimethylamino, generated glassy polymers. Many substituents, such as phenoxy or trifluoroethoxy, yielded polymers that were flexible, film-forming materials. All polymers were stable to water, base, or aqueous acid and did not burn.

The first mixed substituent polymers were reported in 1968 (12) and alternative routes to producing mixed substituent derivatives were developed shortly thereafter (13,14,15).

The relative ease with which a wide variety of polymers, all with different properties, can be synthesized from one precursor (poly(dich-lorophosphazene))(VI) illustrates the unique advantage of the polyphosphazenes. The number of different phosphazene polymers which can be produced appears to be nearly unlimited when one consideres the vast choice of different alcohols, aromatic nucleophiles, primary and secondary amines, etc. which are available to chemists for use as substituents.

CHLOROPHOSPHAZENE HIGH POLYMER SYNTHESIS

The majority of all known phosphazenes, both cyclic and polymeric, are derived from hexachlorocyclotriphosphazene (IV) and the corresponding tetramer octachlorocyclotetraphosphazene (V). These two compounds are formed by the reaction of ammonium chloride with phosphorus pentachloride in a refluxing organic solvent such as chlorobenzene or tetrachloroethane.

$$NH_4Cl + PCl_5 \xrightarrow{-HCl} (NPCl_2)_3 + (NPCl_2)_4$$
$$\text{(IV)} \qquad \text{(V)}$$
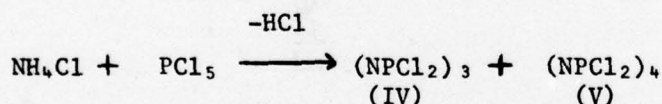
The cyclic trimer and tetramer may comprise 90% of the reaction products, with the trimer predominating, usually in a 3:2 ratio.

Hexachlorocyclotriphosphazene is a white crystalline solid which melts at 113 - 114°C, sublimes in vacuum and is soluble in organic solvents. In aqueous media, hydrolysis of this compound to hydrochloric acid, ammonia and phosphate occurs. Before using it in polymerization reactions, the trimer is usually separated from the tetramer and purified by several vacuum sublimations at 60°C and recrystallizations from a hydrocarbon solvent such as hexane. A final vacuum sublimation is usually carried out just prior to use to ensure that fresh, highly purified trimer is present. These precautions regarding purification of the hexachlorocyclotri-

phosphazene prior to polymerizing it are necessary because of the complexity of the chlorophosphazene polymerization process. Unlike many organic polymerizations, this is a highly unpredictable reaction that is unusually sensitive to the presence of trace impurities. For example, phosphorus pentachloride which is used in the synthesis of the trimer is a powerful polymerization inhibitor and it can be carried through the purification process in trace amounts sufficient to totally block polymerization. It functions mainly by end-capping the growing polymer chain which is being formed by the ring-opening of chlorinated phosphazene cyclics (16,17,18). In addition, traces of water function as a catalyst at low concentrations (~0.1%), and as an inhibitor or crosslinking agent at higher concentrations (18). Even in the apparent absence of impurities, crosslinking of the polymer takes place after about 70-75% of the trimer has been consumed (9,10).

The polymerization is usually carried out by degassing purified hexachlorocyclotriphosphazene by a melt-freeze technique under high vacuum and sealing the material in an evacuated glass tube. The sealed tube is placed in a thermoregulated oven and heated at 245 - 250°C until the molten reaction mixture becomes so viscous that flow ceases (24-72 hours). Agitation of the tubes during polymerization can be carried out to ensure mixing of the contents (19). When cooled to room temperature, a solid plug of white material containing polymer and unreacted trimer is formed. The polymer-trimer mixture is then transferred to a vacuum sublimator, the glass tube opened and most of the trimer removed by sublimation at 50 - 60°C under high vacuum. The remaining poly(dichlorophosphazene) may then be dissolved in dry benzene prior to carrying out substitution reactions. Any crosslinked polymer present will not dissolve and can be separated. If necessary, the chloropolymer may be further purified by precipitation from dry benzene solution into an excess of dry hexane. Once the polymer has been isolated, it normally is used immediately for further reaction because of its hydrolytic instability.

Recently, it was found (20, 24) that linear-type soluble polymers may be obtained by thermal reaction or organocyclotriphosphazenes containing a minimum of three chlorine atoms or by co-polymerization of hexachlorocyclotriphosphazene with hexaorgano-substituted cyclotriphosphazene. The polymers obtained possessed mixed chloro and organic substituents and were hydrolytically unstable. This new route for poly(organophosphazene) synthesis offers promise as an alternative route to producing phosphazene polymers with mixed substituents.

The mechanism of the polymerization reaction is still not understood fully. The electrical conductivity of the molten trimer is known to increase tremendously at temperatures where polymerization occurs (e.g. >230°C). This suggests that ionization of the phosphorus-chlorine bond occurs during initiation or propogation stages (Scheme 3). The catalytic effect of low concentrations of water suggests either that this reagent facilitates removal of chloride ion from phosphorus or that

SCHEME 3.

Suggested Mechanism for Hexachlorocyclotriphosphazene Polymerization.
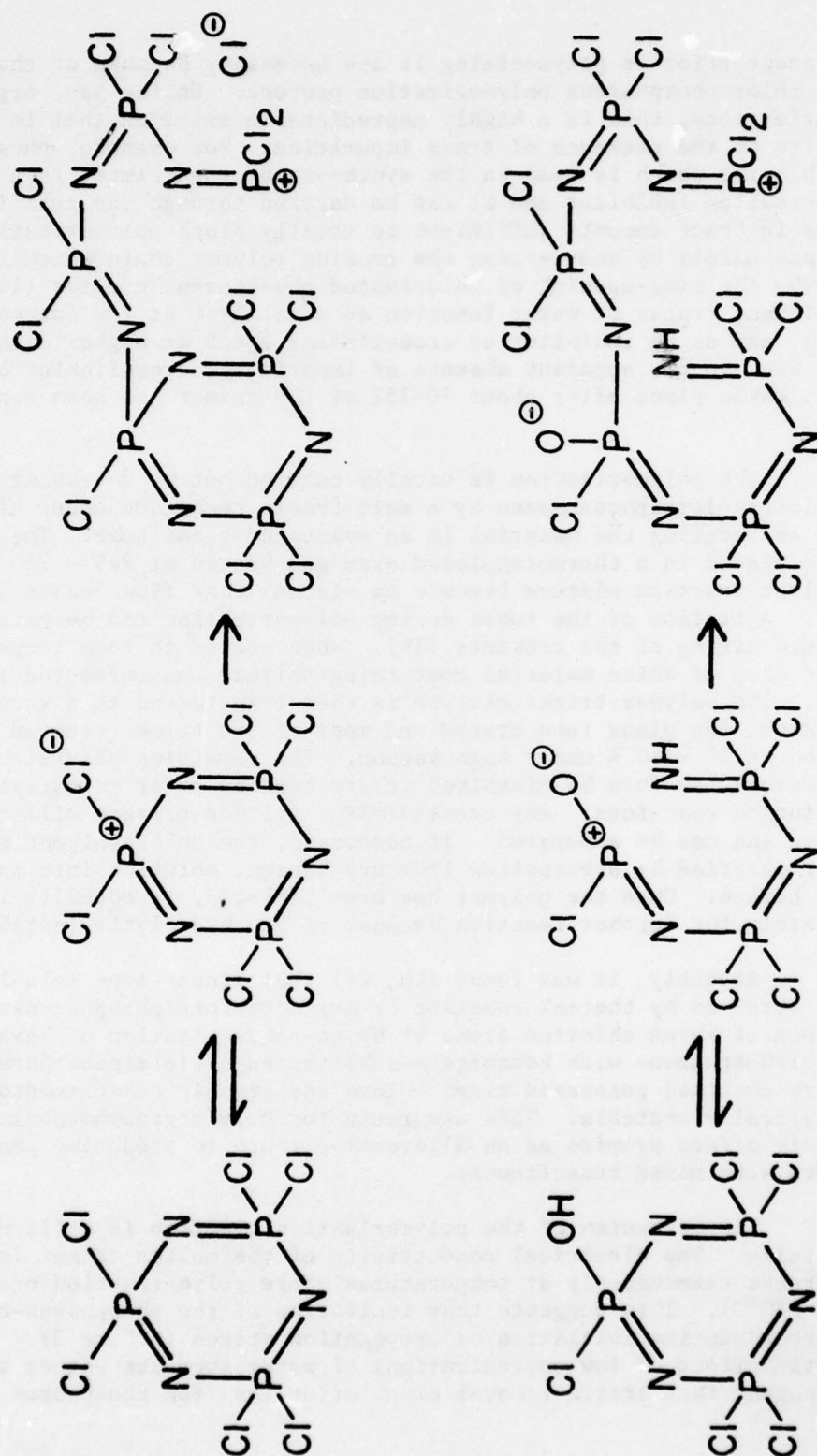
the reaction initiators are hydroxychlorophosphazenes, formed by the replacement of a few P-Cl bonds in the system by P-O-H groups following contact with e.g. atmospheric moisture (16). In any case, the presence of phosphorus-halogen bonds is presumed to be a prerequisite for polymerization (hexafluoro- and hexabromocyclotriphosphazene undergo thermal polymerization similar to the chloro compound). It seems that non-hydrolytic crosslinking does not occur until a deficiency of trimer exists in the polymerization system. This implies that an attack by active chain ends on other growing chains would provide a plausible crosslinking mechanism.

SYNTHESIS OF POLY(ORGANOPHOSPHAZENES)

The wide range of phosphazene polymers containing organic substituents is readily derived from substitution reactions carried out on a single starting material, linear poly(dichlorophosphazene) or its fluoro or bromo analogues. In organic polymer chemistry, the modification of polymers by substitution reactions can only rarely be used as a synthesis route. The coiling of polymer chains in solution and the relatively low reactivity of halogen atoms bonded to a hydrocarbon chain (e.g. polyvinyl chloride) severely restrict the degree to which polymers can be modified. The same holds true for methylsiloxane polymers. The methyl group cannot be replaced effectively by other groups and, therefore, different polymers must each be made by polymerization of the corresponding monomers. Thus, the advantage in poly(organophosphazene) synthesis derives from the use of a single, chemically reactive polymeric species which can be used as an intermediate in the preparation of a multiplicity of stable derivatives.

Alkoxy or aryloxy groups may be introduced into the phosphazene structure quite readily. Homopolymers (phosphazenes containing one type of substituent) are prepared by adding a solution of poly(dichlorophosphazene) in benzene or tetrahydrofuran dropwise to a stirred solution of a slight excess of sodium alkoxide or aryloxide, usually in an ethereal solvent (9,10). After completion of the reaction, the polymer is freed from sodium chloride by washing with water, re-precipitated from e.g. tetrahydrofuran into hexane or benzene to remove unreacted and/or low molecular weight material, dried and then solution-cast as a film or solution-extruded into fibers.

The aminolysis of poly(dichlorophosphazene) is usually accomplished by using an excess of the appropriate amine which functions as a nucleophile and a hydrohalide scavenger (11,13,22,23). Completely substituted poly-(aminophosphazenes) can be synthesized readily using ethylamine, propylamine, butylamine, aniline, piperidine, dimethylamine, etc. (11,22). Ammonia tends to crosslink the chains and the crosslinking process leads to insolubilization and incomplete substitution. Methylamine behaves in a similar manner at room temperature or above but fully substituted linear

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polymers are produced if the reaction is carried out at low temperatures (22). These results indicate that the crosslinking reaction, as shown in Scheme 4, is retarded by increasing the steric bulk of the amine. Beyond a certain size, however, the bulkiness of the N-substituent can create some problems. For example, N-methylaniline does not replace all the halogen atoms in poly(dichlorophosphazene)(22)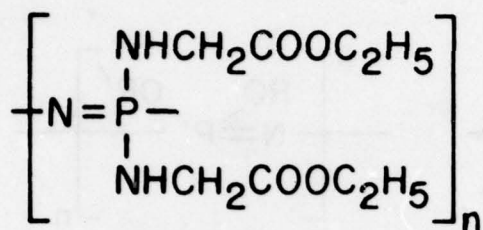 and diphenylamine causes decomposition rather than undergoing the substitution reaction. Diethylamine replaces exactly one half of the available chlorine atoms to yield a surprisingly stable elastomeric polymer which can itself be subjected to further nucleophilic substitution to yield mixed substituent derivatives (13,22).

Recently, a series of flexible polymers that contain amino acid ester units as substituent groups have been synthesized (19). The amino acid groups are bound to the polymer through the amino center. Polymers have also been made which contain both an amino acid ester and a second, water solubilizing group, such as methylamino. Two typical polymers are shown in formulas VII and VIII.
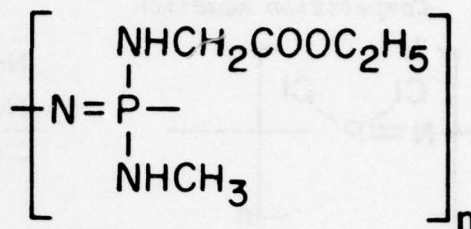
SCHEME 4.

Crosslinking of Poly (dichlorophosphazene) With Ammonia.

$$\left[\begin{array}{c} NHCH_2COOC_2H_5 \\ | \\ -N=P- \\ | \\ NHCH_2COOC_2H_5 \end{array} \right]_n$$

$$\left[\begin{array}{c} NHCH_2COOC_2H_5 \\ | \\ -N=P- \\ | \\ NHCH_3 \end{array} \right]_n$$
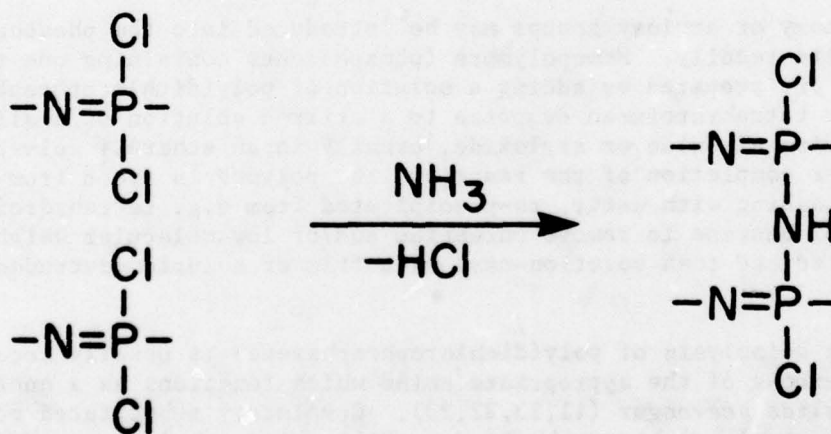
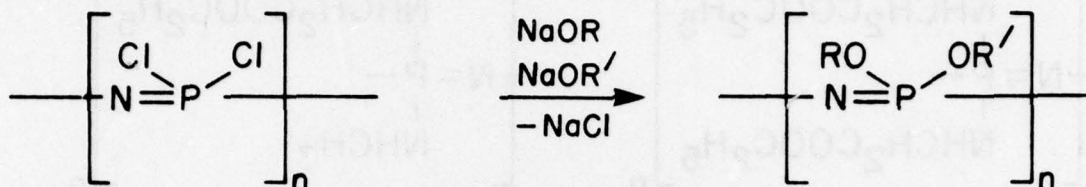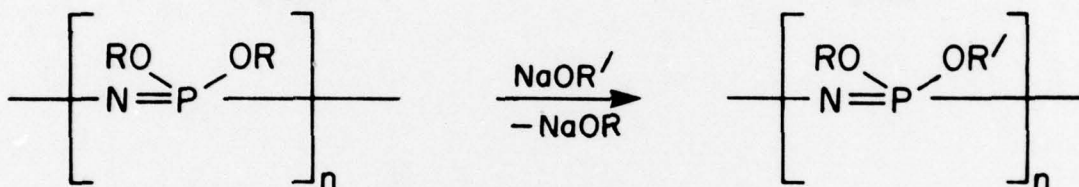<u>VII</u>   <u>VIII</u>

Three different methods are used at present to produce phosphazene polymers containing mixed substituents. Using alkoxy or aryloxy substituents as examples, the first method (12) involves allowing poly(dichlorophosphazene) to react simultaneously with two or more different alkoxides (Scheme 5, equation 1). If the reactivities of the two nucleophiles are similar then their introduction into the polymer will be random. The second way to achieve mixed substitution is illustrated by equation 2, Scheme 5. Treatment of an alkoxyphosphazene homopolymer with the alkali metal salt of a second nucleophile permits a metathetical ligand exchange to take place (25). Elastomers made in this way are similar to those prepared by the direct competition route; however, the ligand exchange route offers some control over the amount of second substituent introduced into the polymer, a problem which is more difficult to resolve via direct competition when the two nucleophiles have vastly different reactivities. Some restrictions exist with respect to the types of alkoxy or aryloxy groups that can be exchanged (15).

The third method, mentioned previously, involves the partial replacement of halogen in poly(dichlorophosphazene) using diethylamine as a sterically-hindered nucleophile. The remaining chlorine atoms may then be replaced by other less-hindered nucleophiles such as methylamine, sodium alkoxides, etc.

SCHEME 5.

Synthesis of Mixed Substituent Poly (organophosphazenes).

(1)   Competition Reaction

$$\left[\begin{array}{c} \text{Cl} \quad\ \text{Cl} \\ \text{N}=\text{P} \end{array}\right]_n \quad \xrightarrow[-\text{NaCl}]{\begin{array}{c}\text{NaOR}\\\text{NaOR}'\end{array}} \quad \left[\begin{array}{c} \text{RO} \quad\ \text{OR}' \\ \text{N}=\text{P} \end{array}\right]_n$$

(2)   Ligand Exchange

$$\left[\begin{array}{c} \text{RO} \quad\ \text{OR} \\ \text{N}=\text{P} \end{array}\right]_n \quad \xrightarrow[-\text{NaOR}]{\text{NaOR}'} \quad \left[\begin{array}{c} \text{RO} \quad\ \text{OR}' \\ \text{N}=\text{P} \end{array}\right]_n$$

The properties of a few selected phosphazene polymers including
the halophosphazene starting materials are listed in Table I. With the
exception of the methoxy- and ethoxy homopolymers which are elastomeric
at 25°C (9,10), most known alkoxy- or aryloxyphosphazene high polymers
are colourless, flexible, film-forming thermoplastics at room temperature.
Some have very low glass transition temperature (Tg), and many are
microcrystalline materials. Oxyphosphazenes are stable to air and moisture
and can be stored in contact with strong aqueous base or aqueous acid
without decomposition unless acid- or base-labile groups are present in
the substituents. Polymers that contain fluoroalkoxy groups are also
water- and oil-repellent. Very few of the known phosphazene polymers
will burn and many can function as flame retardants for organic polymers.
More extensive reviews of the properties of known organo phosphazene
polymers are given elsewhere (3,4).

PROBLEMS IN POLY(ORGANOPHOSPHAZENE) SYNTHESES

One of the major problems encountered in phosphazene polymer
chemistry is the unpredictability of the chlorophosphazene polymerization
reaction. The pure starting material, hexachlorocyclotriphosphazene,
polymerizes at an observable rate at temperatures exceeding 230°C. As
will be discussed later, reactions carried out at temperatures above 250°C
tend to favor depolymerization of polymer to cyclic trimer and oligomers

TABLE I

Properties of Selected Poly(organophosphazenes)

Polymer	Tg (°C)	Tm (°C)	Physical Form at 25°C	Solvent
$[NP(OMe)_2]_n$	−76	−	elastomer	methanol
$[NP(OEt)_2]_n$	−85	−	elastomer	alcohols
$[NP(OCH_2CF_3)_2]_n$	−66	242	flexible thermoplastic	acetone, THF
$[NP(OCH_2(CF_2)_6CF_3)_2]_n$	−40	−	powder	none
$[NP(OPh)_2]_n$	−8	390	flexible film	benzene
$[NP(OC_6H_4Me-m)_2]_n$	−25	348	flexible film	THF, CHCl$_3$
$[NP(NHMe)_2]_n$	14	140	flexible thermoplastic	H$_2$O
$[NP(NHPh)_2]_n$	105	−	glass	benzene
$[NP(OCH_2CF_3)(OCH_2C_3F_7)]_n$	−68	−	flexible thermoplastic	fluorocarbons
$(NPF_2)_n$	−96	−68	elastomer	−
$(NPCl_2)_n$	−63	−30	elastomer	benzene
$(NPBr_2)_n$	−15	270	rubbery thermoplastic	

so that fairly strict control of the reaction temperature is necessary to ensure polymer formation. Prolonged polymerization leads to the formation of crosslinked, insoluble "inorganic rubber" that is unsuitable for substitution reactions; the onset of crosslinking occurs when about 70-75% trimer has reacted and proceeds rapidly and irreversibly. Different batches of trimer obtained from the same source and purified by an identical sequence of operations can nevertheless polymerize at widely differing rates. Thus, it may be possible to standardize the purification and polymerization technique in one laboratory but other laboratories may experience remarkably different experimental results. Some of these problems stem from the presence of trace impurities such as water and phosphorus pentachloride which can affect greatly the outcome of the polymerization reaction (16).

A second problem in phosphazene polymer chemistry is related to the high-temperature behavior of many derivatives. Aminophosphazene polymers decompose at high temperatures (e.g. 300°C) to yield side-group fragments with concurrent crosslinking of the chains. Like polysiloxanes, alkoxy and aryloxyphosphazene polymers tend to depolymerize at temperatures above 250°C. Unlike aminopolyphosphazenes, the oxyphosphazene derivatives yield small cyclic phosphazenes that have the same basic repeating structure as the high polymer (26,27). The depolymerization reaction is a response to thermodynamic factors (4); at high temperatures, the formation of numerous small molecules is entropically favoured over the production of a few long chain molecules. This factor is responsible also for the high-temperature depolymerization of organic polymers, such as poly(methylmethacrylate) to their vinyl monomers. Poly(dimethylsiloxane) depolymerizes for the same reason.

In addition, bulky organic substituents on the phosphazene polymer chain create intramolecular steric hinderance in the polymer which can be relieved by formation of cyclic trimer or tetramer via depolymerization, as is similar to the case with organic polymers and silicones.

These thermodynamic instabilities do not necessarily mean that poly(organophosphazenes) have poor thermal stability and, in practice, the phosphazenes show no worse thermal stability than silicones or most organic polymers. Crosslinking of the chains, the absence of chloro, P-OH or NH groups or the introduction of discontinuties such as phenyl substitutents in alkoxy or aryloxyphosphazenes all serve to raise thermal stability.

A third problem is related to steric hindrance during the substitution reactions. The rate of halogen replacement in poly(dichlorophosphazene) decreases when bulky nucleophiles are employed. For example, when diphenylamine is used as a reagent, no substitution occurs at all (14). As discussed previously, diethylamine replaces only half the available

chlorine and N-methylaniline replaces even fewer chlorines. The substitution process appears to be an S_N2-type replacement reaction with the well-known steric effects that are encountered in this type of reaction.

Although the majority of alkoxyphosphazene polymers are extremely stable as solids and in solution, the lower homologues can undergo rearrangements under relatively mild conditions. For example, it has been reported (28,29,30) that hexamethoxycyclotriphosphazene (IX) rearranges to the corresponding trioxycyclotriphosphazene (X) upon distillation under vacuum. The cyclic tetramer undergoes a similar rearrangement. These reactions, which involve the migration of a methyl group from the methoxy position to the adjacent nitrogen center, are shown in Scheme 6. This type of rearrangement can also take place in high molecular weight poly(dimethoxyphosphazene). For example, heating the solid polymer at 130 °C for 6 hours results in approximately 35% conversion to the N-methyl form (31). Qualitative evidence has been obtained which indicates that the ethoxy homologue, (poly)diethoxyphosphazene, depolymerizes slowly in ethanol solution at 25 °C (10).

TECHNOLOGICAL APPLICATIONS OF POLY(ORGANOPHOSPHAZENES)

The successful preparation of a wide variety of stable poly(organo-phosphazene) derivatives which exhibit unique combinations of physical properties has created promising technological prospects for these polymers. Current interest and activity is focused on four main areas as follows:

EXTREME-SERVICE APPLICATIONS

Certain mixed substituent phosphazene elastomers have important advantages over poly(dimethylsiloxane) or conventional organic elastomers, especially with respect to combined solvent resistance and low-temperature elasticity. For example, a poly(phosphazene) containing mixed trifluoro-ethoxy and fluoropentoxy substituents developed by the Firestone Tire and Rubber Company (PNF elastomer) shows excellent resistance to oils, fuels and hydraulic fluids and has a service temperature range of -60 °to 200 °C. Thus, such material makes an outstanding candidate for arctic fuel hoses, oil seals, gaskets etc. in critical automotive, aerospace, military, industrial and oil exploration applications. (6,25,33,34,35). A description of the processing and rheological characteristics of this type of fluoroalkoxy-phosphazene has been published (25). The solution properties of several fluorophosphazene elastomers have also been studied (32).

SCHEME 6.

Methyl Group Migration In Methoxy Phosphazenes.
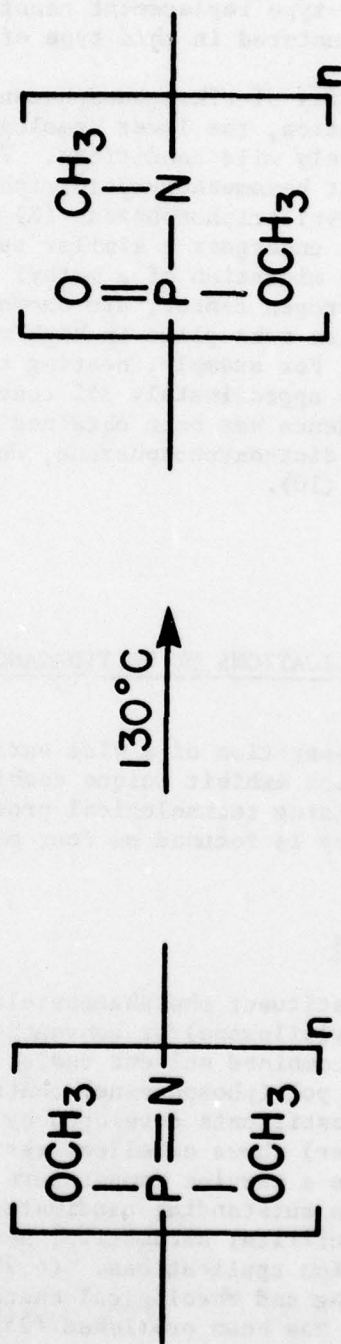
SURFACE COATINGS

The film-forming poly(phosphazenes) offer some advantages over conventional organic films. Combined with their inherent flame resistance, the polymers can be carefully designed to have specific surface characteristics, adhesion properties or solvent insolubility. Because the polyphosphazene backbone does not absorb ultraviolet light at wavelengths longer than 200 nm, the weathering stability of polyphosphazenes can be expected to exceed that of organic polymers. In general, film-forming poly(aryloxyphosphazenes) are also resistant to air oxidation, are unaffected by moisture and many retain their flexibility at temperatures as low as -80°C. Therefore, applications such as outdoor surface coatings or wire coatings are feasible.

One of the major areas of study at the present time is the use of polyphosphazenes as fire-resistant coatings. For example(36), a fluorinated poly(phosphazene) derivative has been evaluated for use as a surface coating for the U.S. Army Self-Contained, Transportable Medical Unit Shelter. The outer layer of the shelter is made from polyester fabric which is usually coated on both sides with polychloroprene and top coated on the outside with chlorosulfonated polyethylene to provide fire resistance. When coated with poly(phosphazene), laboratory flammability tests showed the material to be superior to the chloroprene/chlorosulphonate coated material and gave indications of better flame resistance and lower fire propagation in an actual fire situation (36). Other types of phosphazene polymers, in particular homo- and copolymers of aryloxyphophazenes, have been developed and investigated as fire-resistant coatings and foams for use in submarines, for example (37,38). In tests conducted so far, very low levels of toxic products have been detected in combustion studies on poly(aryloxyphosphazenes)(38).

TEXTILE TECHNOLOGY

Most phosphazene polymers can be easily fabricated into monofilaments and thus textiles form a logical area for future uses of the polyphosphazenes. Specific homopolymers such as poly[bis(trifluoroethoxy)phosphazene] impart water- and oil-repellent properties when applied to fabrics and can be dyed or substituted with dye molecules. Work in progress at DREO indicates that alkoxy phosphazene polymers containing mixed fluorinated and hydrocarbon substituents impart high levels of water and oil repellency to fabrics and are non-burning, thus conferring some flame resistance to the fabric as well (39). Because polyphosphazenes are still relatively expensive at present, their initial development in the textile field would likely be as fibers for fire-resistant fabrics (e.g. racing driver uniforms, aircrew garments, etc.) or for co-weaving with conventional organic polymer fibers.

BIOMEDICAL APPLICATIONS

Square planar platinum complexes have been intensively investigated as anti-cancer drugs (40). However, these compounds are rapidly excreted from the body which limits their effective chemotherapeutic use. In contrast, water-soluble high polymers cannot pass through semi-permeable membranes (such as those of the kidney) and thus are retained within the circulatory system and are not excreted. A drug molecule bound to such a polymer should be similarly retained until decomposition of the polymer permitted its slow controlled release. Therefore water-soluble phosphazene polymer complexes of the type $[NP(NHCH_3)_2]_4PtCl_2$ have been prepared in which dichloro platinum ligands are bound to the skeletal nitrogen atoms of the phosphazene chain (41,42). These complexes have proved to be effective antitumor agents. The pure polymer itself functions as a powerful blood anticoagulant. Polyaminophosphazenes have also been used to form a complex with iron (Fe^{3+}) porphorin complexes, such complexes forming reversible oxygen binding systems which may have long-range uses as blood transfusion substitutes.(4).

Some work involving phosphazenes has been carried out in the insect control field. For example, butoxyphosphazenes are toxic to aphids. The cyclic compound hexakis(ethyleneimino)cyclotriphosphazene is useful as a chemosterilant for houseflies and other insects (43).

In general, the extreme water-repellency of certain alkoxy- and aryloxy poly(phosphazenes), coupled with high elasticity and low fat absorption, makes them ideal candidates for the fabrication of or for coating biomedical replacement devices, such as articifial heart pumps. In initial blood and tissue compatibility tests, the polyphosphazenes appear to be superior to silicone rubber or conventional organic polymers when used as implants.

Polyphosphazenes may also be useful in the field of biodegradable polymers. For example, there exists a need for a synthetic surgical suture material which will degrade slowly in the body and produce innocuous products. There is also a need for polymers that can be used to replace body parts but will degrade slowly and disappear as new cell growth takes place. To meet these needs, a class of polyphosphazenes bearing amino acid ester substituents has been synthesized (19). A typical example of this class is poly[bis(ethylglycinato)phosphazene], a tough leathery material which degrades slowly under aqueous conditions to an amino acid, phosphate and ammonia. By introducing bulkier amino acid residues, such as alanine or leucine esters, the polymer can be designed to undergo molecular weight decline and dissolution spontaneously at body temperature over a period of several weeks. The polymer can be stored indefinitely at low temperatures.

SUMMARY

Poly(organophosphazenes) are a new class of polymers that have an exciting future as technological elastomers, films, fibers, textile treatments and as reconstructive plastics or slow-release agents and drug carriers in biomedicine. An almost unlimited range of phosphazene polymers with unique physical properties may be readily synthesized from a single precursor, linear poly(dichlorophosphazene). Because of the broad versatility of the chlorophosphazene polymer substitution reaction, it is expected that new organophosphazenes will be synthesized to meet specific demands in the future. Poly(phosphazenes) are especially attractive for high performance applications where conventional organic polymers or silicones are unsatisfactory. Thus, these new polymers will find use as gaskets, fuel lines and flexible hoses, electrical insulators, flame-proof plastics, specialty textiles and foams and as biomedical implantation materials. The polymers themselves are derived only in part from petroleum-based chemicals, with readily available ammonium chloride and phosphorus pentachloride forming the basis of the phosphazene chain.

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The poly(organophosphazenes) are a new class of high polymers based on an "inorganic" backbone of alternating phosphorus and nitrogen atoms. These polymers show considerable promise in meeting materials requirements that cannot be met by conventional organic polymers.

In this report, the history of phosphazene polymer development is briefly reviewed, the synthesis and properties of poly(organophosphazenes) are described and some of the problems associated with their synthesis are outlined. The potential technological applications of these polymers as extreme-service materials, protective coatings, textile products and biomedical materials, are also described.

KEY WORDS

Inorganic Polymers
Phosphonitrile Halides
Synthetic Elastomers
Utilization
Polymerization
Chemical Reactions

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